

Application Number 10/549494

Response to the Office Action dated October 16, 2008 and the Advisory Action dated March 6, 2009

### REMARKS

Favorable reconsideration of this application is requested in view of the following remarks.

Claim 1 has been amended to include the limitations of claim 8. Accordingly, claim 8 has been canceled without prejudice.

Claim 28 has been rejected under 35 U.S.C. 112, second paragraph, as being indefinite. Claim 28 has been canceled in the Amendment and Response filed on February 17, 2009, and accordingly, this rejection is moot and should be withdrawn. Applicants do not concede the correctness of the rejection.

Claims 1, 3-7, 9-12, 17, 18, 20, and 26 have been rejected under 35 U.S.C. 103(a) as being unpatentable over Kawamura et al. ("Growth of a large GaN single crystal using the liquid phase epitaxy (LPE) technique") (Kawamura I) in view of Yamada et al. (U.S. Patent No. 5,366,552). Applicants respectfully traverse this rejection.

Kawamura I discloses use of Na flux solution system to grow GaN crystals (see page L4, the left coln., third paragraph). Kawamura I further discloses that the crucible is heated to 800°C while the pressure was increased to a fixed value (see page L4, left coln., third para. to right coln., line 2) but suggests that the crucible is cooled and that controlling temperature is not important because growth of GaN proceeds with dissolution of the high-pressure nitrogen gas into a solution system (see page L4, right coln., third para. lines 1-4. In addition, Kawamura I fails to disclose that the flux is stirred by rocking the reaction vessel and simultaneously is heated in addition to the heating for preparation of the flux as claim 1 requires. By a combination of thermal convection and mechanical stirring, purity of the crystal is increased, and a surface of the crystal becomes smooth (see page 7, lines 7-26 of the specification and Figs. 7a and 7b at page 6 of "Growth of high-quality large GaN crystal by Na flux LPE method" ("SPIE reference") presented at the conference of SPIE Photonics West 2009 attached to the Amendment and Response filed on February 17, 2009. Further, by the combination of

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thermal convection and mechanical stirring, a transparent GaN crystal is obtained (see page 2, lines 12-17 of the specification). In contrast, the GaN crystal produced by only mechanical stirring shows a brown color (see Kawamura et al. "Novel Liquid Phase Epitaxy (LPE) Growth Method for Growing Large GaN Single Crystals: Introduction of the Flux Film Coated-Liquid Phase Epitaxy (FFC-LPE) Method" Jpn. J. Appl. Phys. Vol. 42 (2003), pp. L 879 – L 881 at page 881, left coln. first para. lines 6-8, which was filed on May 23, 2008 as the Information Disclosure Statement document and attached hereto for the Examiner's convenience). Such improvement of the properties of the crystals by stirring and heating simultaneously cannot be expected from Kawamura I.

Yamada discloses a growth chamber that is rotated (see abstract). Yamada, however, does not suggest that the step of stirring and heating the crystals simultaneously in addition to the heating for preparation of the flux improves the properties of the crystals and does not remedy the deficiencies of Kawamura I.

D'Evelyn et al. (U.S. Patent No. 6,398,867), which has been cited for rejection of claim 8, discloses a manufacturing method of a crystalline gallium nitride by subjecting a capsule including a source gallium nitride, a mineralizer, and a solvent to heat and pressure in order to dissolve the source gallium nitride, i.e., producing a flux, cooling the system, and relieving the capsule from the high pressure and temperature (see abstract). D'Evelyn fails to disclose that the flux in which the source gallium nitride is dissolved is stirred by rocking and heated in addition to the heating for preparation of the flux while the crystal is growing as claim 1 requires and fails to suggest the unexpected improvement of the properties of the crystal by the combination of rocking and heating. Thus, D'Eveln also does not remedy the deficiencies of Kawamura I. In addition, in D'Eveln, free convection is impeded by a baffle structure (18), which acts as a partial barrier, and convection is limited in each of end units (1) and (2) (see Fig. 5 and coln. 7, lines 38-50). In contrast, Kawamura I requires nitrogen gas in a Na flux solution for growth of the GaN crystals, and there is no reasonable basis to combine Kawamura I with D'Eveln.

Accordingly, claim 1 is distinguished from Kawamura I in view of Yamada, and the rejection should be withdrawn.

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Claim 8 has been rejected under 35 U.S.C. 103(a) as being unpatentable over Kawamura et al. ("Growth of a large GaN single crystal using the liquid phase epitaxy (LPE) technique") (Kawamura I) in view of Yamada et al. (U.S. Patent No. 5,366,552) and further in view of D'Evelyn et al. (U.S. Patent No. 6,398,867). Applicants respectfully traverse this rejection.

Claim 8 has been canceled, and the limitations of claim 8 has been included in claim 1 as discussed for claim 1 above. Thus, this rejection is moot and should be withdrawn.

Claim 14 has been rejected under 35 U.S.C. 103(a) as being unpatentable over Kawamura et al. ("Growth of a large GaN single crystal using the liquid phase epitaxy (LPE) technique") (Kawamura I) in view of Yamada et al. (U.S. Patent No. 5,366,552), and further in view of Kawamura et al. (Synthesis of bulk GaN single crystals using Na-Ca flux) (Kawamura II). Applicants respectfully traverse this rejection.

Claim 14 is distinguished from Kawamura I in view of Yamada for at least the same reasons as discussed for claim 1 above. Kawamura II neither discloses a step of stirring the flux by rocking and heating simultaneously in addition to the heating for preparation of the flux nor suggests the unexpected improvement of the properties of the crystal by the combination of rocking and heating, and Kawamura II does not remedy the deficiencies of Kawamura I in view of Yamada. Thus, the rejection should be withdrawn. Applicants do not concede the correctness of the rejection for the features of claim 14.

Claims 21 and 24-25 have been rejected under 35 U.S.C. 103(a) as being unpatentable over Kawamura et al. ("Growth of a large GaN single crystal using the liquid phase epitaxy (LPE) technique") (Kawamura I) in view of Yamada et al. (U.S. Patent No. 5,366,552), and further in view of Shibata et al. (U.S. Patent No. 6,270,569). Applicants respectfully traverse this rejection.

Claims 21, 24, and 25 are distinguished from Kawamura I in view of Yamada for at least the same reasons as discussed for claim 1 above. Shibata neither discloses a step of stirring the flux by rocking and heating simultaneously in addition to the heating for

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preparation of the flux nor suggests the unexpected improvement of the properties of the crystal by the combination of rocking and heating, and Shibata does not remedy the deficiencies of Kawamura I in view of Yamada. Thus, the rejection of claims 21, 24, and 25 should be withdrawn. Applicants do not concede the correctness of the rejection for the features of claims 21, 24, and 25.

Claim 27-28 have been rejected under 35 U.S.C. 103(a) as being unpatentable over Kawamura et al. ("Growth of a large GaN single crystal using the liquid phase epitaxy (LPE) technique") (Kawamura I) in view of Yamada et al. (U.S. Patent No. 5,366,552), and further in view of Hawrylo et al. (U.S. Patent No. 3,811,963). Applicants respectfully traverse this rejection.

Claim 28 has been canceled. Claim 27 is distinguished from Kawamura I in view of Yamada for at least the same reasons discussed for claim 1 above. Hawrylo neither discloses a step of stirring the flux by rocking and heating simultaneously in addition to the heating for preparation of the flux nor suggests the unexpected improvement of the properties of the crystal by the combination of rocking and heating, and Hawrylo does not remedy the deficiencies of Kawamura I in view of Yamada. Thus, the rejection should be withdrawn. Applicants do not concede the correctness of the rejection for the features of claims 27 and 28.

Claim 30 has been rejected under 35 U.S.C. 103(a) as being unpatentable over Kawamura et al. ("Growth of a large GaN single crystal using the liquid phase epitaxy (LPE) technique") (Kawamura I) in view of Yamada et al. (U.S. Patent No. 5,366,552), and further in view of Inoue et al. (Japanese Examined Patent Application Publication No. 75-11870). Applicants respectfully traverse this rejection.

Claim 30 is distinguished from Kawamura I in view of Yamada for at least the same reasons discussed for claim 1 above. Inoue neither discloses a step of stirring the flux by rocking and heating simultaneously in addition to the heating for preparation of the flux nor suggests the unexpected improvement of the properties of the crystal by a combination of rocking and heating, and Inoue does not remedy the deficiencies of

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Kawamura I in view of Yamada. Thus, the rejection should be withdrawn. Applicants do not concede the correctness of the rejection for the features of claim 30.

Claims 1, 3-12, 14, 17-18, 20-21, 24-28, and 30 have been rejected on the ground of nonstatutory obviousness type double patenting as being unpatentable over claims 1-36 of copending Application No. 11/661,013. Applicants respectfully traverse this rejection.

As discussed in the Amendment and Response filed on February 17, 2009, the express abandonment of Application No. 11/661,013 was submitted on February 13, 2009. Accordingly, this rejection is moot and should be withdrawn. Applicants do not concede the correctness of this rejection.

In view of the above, Applicants request reconsideration of the application in the form of a Notice of Allowance.



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DPM/my/ad

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## Novel Liquid Phase Epitaxy (LPE) Growth Method for Growing Large GaN Single Crystals: Introduction of the Flux Film Coated-Liquid Phase Epitaxy (FFC-LPE) Method

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We developed a new liquid phase epitaxy (LPE) growth method for growing large GaN single crystals. In this method, the homo-epitaxial growth of the GaN crystal proceeds by nitrogen dissolution against a Na-Ga solution film coating the GaN thin-film substrate. A growth rate of 4  $\mu\text{m/h}$  was achieved though nitrogen pressure was relatively low at 9.5 atm. Furthermore, the GaN film grown by this method showed a flat surface. [DOI: 10.1143/JJAP.42.L879]

**KEYWORDS:** GaN, LPE, single crystal, photoluminescence, bulk

GaN-based short wavelength optical devices have been fabricated mainly on sapphire substrates, which generates many dislocations in the fabricated film resulting from large misfits between the substrate and growing film. Dislocations in the films deteriorate their emitting properties, including their efficiency or lifetimes. These problems resulting from dislocations seem to be solved by fabricating such devices on GaN substrates that include few dislocations.<sup>1)</sup> Therefore, many researchers have been developing growth methods with the aim of growing large GaN single crystals that have low levels of dislocations. Although the hydride vapor phase epitaxy (HVPE) method has enabled us to grow large GaN single crystals, the order of  $10^6 \text{ cm}^{-2}$  or more dislocation density is generated in grown crystals.<sup>2)</sup> On the other hand, the growth of GaN crystals with extremely low dislocations has been successfully achieved by the high-pressure growth method, in which the growth of GaN proceeds in Ga melt.<sup>3,4)</sup> However, the high-pressure growth method has some disadvantages in its application to industrial use, such as its necessity for extremely high nitrogen pressure (more than 10,000 atm) and high growth temperature (more than 1,500 degree C) and its relatively low growth rate. The development of the Na flux method could lower the required pressure to grow the GaN single crystals in a solution system.<sup>5)</sup> In this method, the addition of Na to Ga melt promotes nitrogen dissolution, which results in the low pressure (about 50 atm) growth of GaN single crystals in Ga-based solution. However, the Na flux method also involves the following problems: 1) Crystals grown by this method are easily colored; 2) Growth rate is low, making it difficult to grow large-size crystals; 3) Nucleation frequency in solution is high.<sup>6-8)</sup> We have reported that the changing the flux composition to a Ca-Na or Li-Na flux system showed some advantages, such as drastic increase of yield of GaN and easy synthesizing of the transparent crystals and that application of the liquid phase epitaxy (LPE) technique could grow the large-size GaN single crystals having extremely low dislocations.<sup>9-12)</sup> In this paper, we describe the new LPE method and introduce the advantages of this method for the growth of GaN at a high growth rate and with a large surface area.

Schematic illustrations of the experimental setup and growth program are shown in Figs. 1 and 2, respectively. 15  $\mu\text{m}$  thick-GaN film ( $15 \times 10 \text{ mm}$ ) synthesized by metal-

organic chemical vapor deposition (MOCVD) was set at one side of a BN crucible with an inner diameter of 80 mm. The MOCVD-GaN film was fixed in the groove engraved on the crucible. Na (5.77 g) and Ga (2.0 g) were then set on the

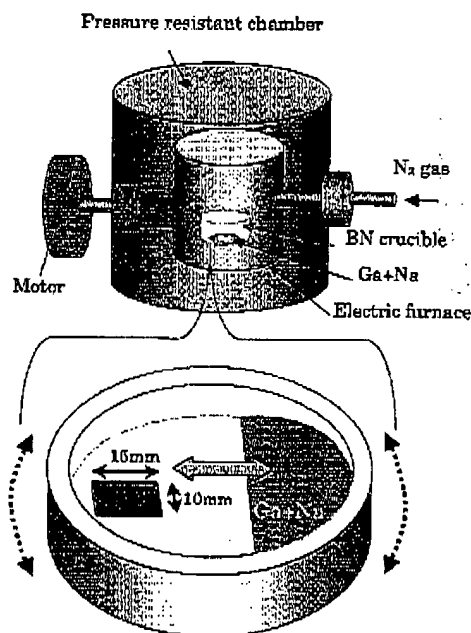


Fig. 1. Schematic illustration of the experimental setup used in this experiment and detailed drawing of reacting portion.

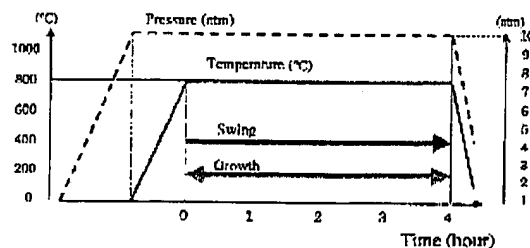


Fig. 2. Growth programs of each parameter such as pressure, temperature, and movement of reacting portion.

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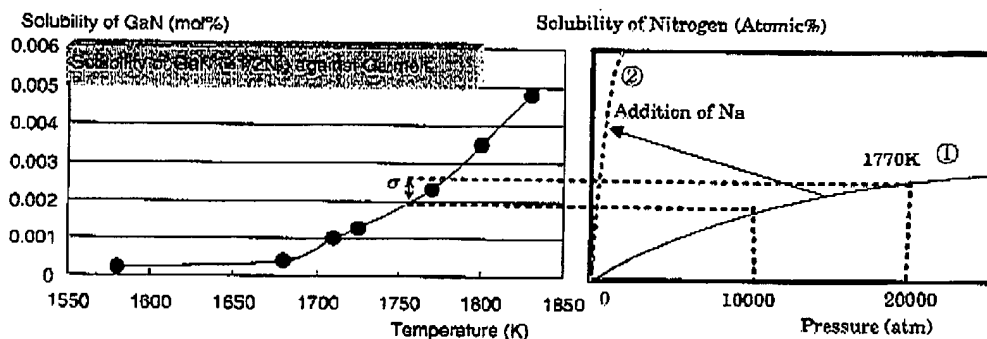


Fig. 3. Diagrammatic explanation of pressure required to grow GaN using the high-pressure solution growth method. The left graph shows the solubility curve of GaN in Ga melt. The right graph shows the changes in the amount of nitrogen gas in Ga melt by varying the applied pressure.

other side of the crucible setting the MOCVD-GaN film. The Boron Nitride (BN) crucible filled with starting materials was transferred into an electric furnace which was placed in a temperature- and pressure-resistant chamber. The electric furnace can be swung by an electric motor periodically in the manner of a pendulum. The electric furnace was placed in a chamber pressurized to 9.5 atm by supplying high purity nitrogen gas. On this occasion, the inside of the electric furnace was also pressurized to 9.5 atm. Next, after the crucible was heated to 800 deg C, the electric furnace was begun to swing in order to move the solution as shown in Fig. 1. The swing rate was 1.5 times per minute. MOCVD-GaN film was continually covered with the flux solution film containing Ga. LPE-GaN crystal grew on the MOCVD-GaN due to nitrogen dissolution into the solution film covering the MOCVD-GaN for 4 h.

In the Na flux method, crystal growth proceeds by continuous dissolution of pressurized nitrogen gas into the Na-Ga solution system at a constant temperature. This growth mechanism is basically the same as the high-pressure solution growth method, whereas more than 10,000 atm is required by the high-pressure solution growth method. In other words, the high-pressure solution growth method can be regarded as growing GaN in a Ga self-flux. Porowski *et al.* have reported the nitrogen concentrations in the Ga melt when the crystallization of GaN starts.<sup>13)</sup> The nitrogen concentration is approximately the same as the solubility of GaN in solution. For example, it has been reported that 10,000 atm is required to grow GaN at 1770 K. If the amount of nitrogen dissolution due to pressurization obeys the Sieverts law, the nitrogen solubility curve can be indicated as in the right graph shown in Fig. 3. Accordingly, the solubility curve of GaN in Ga melt and the nitrogen solubility curve can be indicated as seen in the left and right graphs of Fig. 3, respectively.<sup>14)</sup> When the value of the right graph exceeds the value of the left graph as a result of pressurization, the crystal can grow; in other words, this is the "threshold pressure". Therefore a pressure of 20,000 atm generates the supersaturation of  $\sigma$  ( $\approx 41\%$ ) indicated in Fig. 3 under a assumption that equilibrium is maintained as growth proceeds. The growth of GaN using the Na flux method is controlled by the same mechanism. The reason that threshold pressure to grow GaN in the Na flux method is

rather lower than that of the high-pressure solution growth method seems to be the drastic promotion of nitrogen dissolution by the existence of Na, which is indicated by the arrow in Fig. 3. The detailed mechanisms of nitrogen dissolution will be reported in our next paper.

The growth rate of GaN by means of the Na flux method is controlled by nitrogen dissolution at the gas-liquid interface. Therefore, the inhomogeneity of the nitrogen concentration in the solution cannot be avoided since the nitrogen concentration at the gas-liquid interface should be higher than the other portion. In addition, the longer the distance from the gas-liquid interface, the lower the growth rate, due to the low nitrogen diffusion rate. It has been reported that the amount of GaN grown near the interface is much higher than that grown in the other portion. Crystals grown in Na flux are apt to have nitrogen vacancies since growth proceeds with nitrogen dissolution to the solution including a large amount of Ga.<sup>15,16)</sup> Accordingly, a high growth rate, homogeneous growth, and a decrease in nitrogen vacancies seem to be achieved by growth just under the gas-liquid interface. We attempted homo-epitaxial growth on a MOCVD-GaN film substrate using Na flux while flux solution film covered the substrate. A schematic illustration of this experiment is shown in Fig. 4. The most important aspect of this growth method is that the surface of the seed crystal is always covered by flux solution film in the

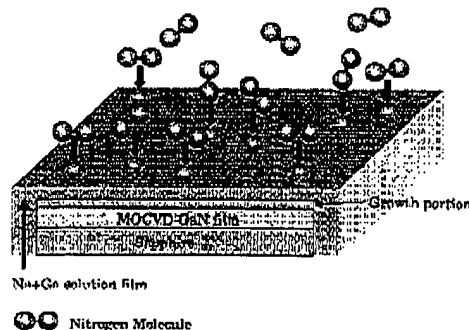


Fig. 4. Schematic illustration of the dissolution of nitrogen gas into the flux solution film.

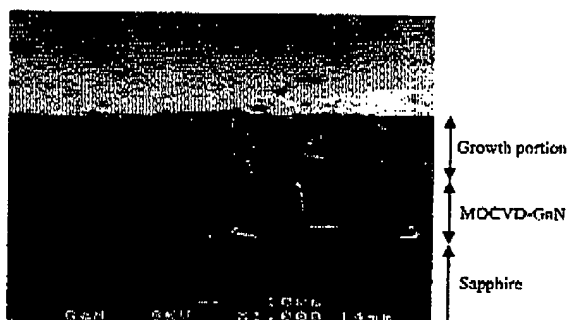


Fig. 5. Cross-sectional SEM image of GaN thin film grown using the FFC-LPE method.

growth period in order to promote the dissolution of reaction gas, which differs fundamentally from the tipping method. We call this growth method the "Flux Film Coated LPE method (FFC-LPE)". Although in the present study we applied this method to the growth of GaN, FFC-LPE can be applied to the growth of many kinds of crystals, in which gas compounds can be used as a source material. It is thought that various compounds which cannot be grown in solution due to the absence of suitable flux or to a limited growth temperature can be grown continuously by this method because the crystals were continuously grown at a constant temperature.

Figure 5 shows the cross-sectional scanning electron microscopy (SEM) image of LPE-GaN film grown by the FFC-LPE method for 4 hours under the conditions of 800 deg C, 9.5 atm, and a swing rate of 1.5 times per minute. 15-μm-thick LPE-GaN film was grown on 15-μm-thick MOCVD-GaN film. The color of the grown film was light brown, which seemed to indicate that the grown film has a high number of nitrogen vacancies. Considering that a threshold pressure of about 20 atm in Na flux has been reported, growth just under the gas-liquid interface showed the effects of the decrease of the pressure required to grow GaN. In this experiment, a growth rate of 4 μm/h was achieved in spite of a low growth pressure of 9.5 atm. Yamane *et al.* reported that 300 hours were needed to grow platelet GaN having dimensions of 10 × 4 × 0.1 mm under 50 atm.<sup>17)</sup> In LPE growth, the growth rate is controlled by the rate along the c-axis because the plane size is determined by the size of the substrate used. Although very rough surface had been produced using the conventional LPE method, the surface morphology of GaN crystals obtained by the FFC-LPE method is almost flat, with many small rugged

facets being confirmed by optical microscope. This improvement of surface morphology is regarded as one of the effects of growing the film just under the gas-liquid interface.

Photoluminescence measurement showed that the GaN film grown using FFC-LPE has a band-edge emission at 361 nm. The measurement was carried out using the 10 mW He-Cd laser as a pumping source. We will report the effect of other fluxes, growth temperatures, and detailed growth mechanisms in other papers.

1) We developed a new growth method, called the Flux Film Coated-LPE (FFC-LPE) method, in which crystal grows in a flux solution film coating the seed.

2) A growth rate of 4 μm was achieved using FFC-LPE under a low nitrogen pressure of 9.5 atm.

3) GaN film having a nearly flat surface could be grown on the MOCVD-GaN substrate using FFC-LPE.

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- 1) Z. Yu, M. A. L. Johnson, J. D. Brown, N. A. El-Masry, J. W. Cook, Jr. and J. F. Schetzina: *J. Cryst. Growth* **195** (1998) 333.
- 2) K. Motoki, T. Okahisa, S. Nakahata, N. Matsumoto, H. Kimura, H. Kasai, K. Takemoto, K. Uematsu, M. Ueno, Y. Kumagai, A. Koukito and H. Seki: *J. Cryst. Growth* **237-239** (2002) 912.
- 3) S. Porowski: *J. Cryst. Growth* **166** (1996) 583.
- 4) I. Grzegory, M. Bockowski, B. Lucznik, S. Krukowski, Z. Romanowski, M. Wroblewski and S. Porowski: *J. Cryst. Growth* **246** (2002) 177.
- 5) H. Yamane, M. Shimada, S. J. Clarke and F. J. DiSalvo: *Chem. Mater.* **9** (1997) 413.
- 6) M. Aoki, H. Yamane, M. Shimada, T. Sekiguchi, T. Hanada, T. Yano, S. Sarayama and F. J. DiSalvo: *J. Cryst. Growth* **218** (2000) 7.
- 7) S. E. Park, C.-R. Cho, S. K. Kim and S.-Y. Jeong: *J. Korean Phys. Soc.* **42** (2003) S161.
- 8) T. Iwahashi, F. Kawamura, M. Morishita, Y. Kai, M. Yoshimura, Y. Mori and T. Sasaki: *J. Cryst. Growth* **253** (2003) 1.
- 9) F. Kawamura, M. Morishita, T. Iwahashi, M. Yoshimura, Y. Mori and T. Sasaki: *Jpn. J. Appl. Phys.* **41** (2002) L1440.
- 10) F. Kawamura, T. Iwahashi, K. Omae, M. Morishita, M. Yoshimura, Y. Mori and T. Sasaki: *Jpn. J. Appl. Phys.* **42** (2003) L4.
- 11) M. Morishita, F. Kawamura, T. Iwahashi, M. Yoshimura, Y. Mori and T. Sasaki: *Jpn. J. Appl. Phys.* **42** (2003) L565.
- 12) F. Kawamura, T. Iwahashi, M. Morishita, K. Omae, M. Yoshimura, Y. Mori and T. Sasaki: *Jpn. J. Appl. Phys.* **42** (2003) L729.
- 13) S. Porowski and I. Grzegory: *J. Cryst. Growth* **178** (1997) 174.
- 14) F. Kawamura, T. Iwahashi, M. Morishita, K. Omae, M. Yoshimura, Y. Mori and T. Sasaki: *Jpn. J. Assoc. Cryst. Growth* **30** (2003) 96 [in Japanese].
- 15) R. B. Zetterstrom: *J. Mater. Sci.* **5** (1970) 1102.
- 16) J. Karpinski, J. Jun and S. Porowski: *J. Cryst. Growth* **66** (1984) 1.
- 17) M. Aoki, H. Yamane, M. Shimada, S. Sarayama and F. J. DiSalvo: *J. Cryst. Growth* **242** (2002) 70.